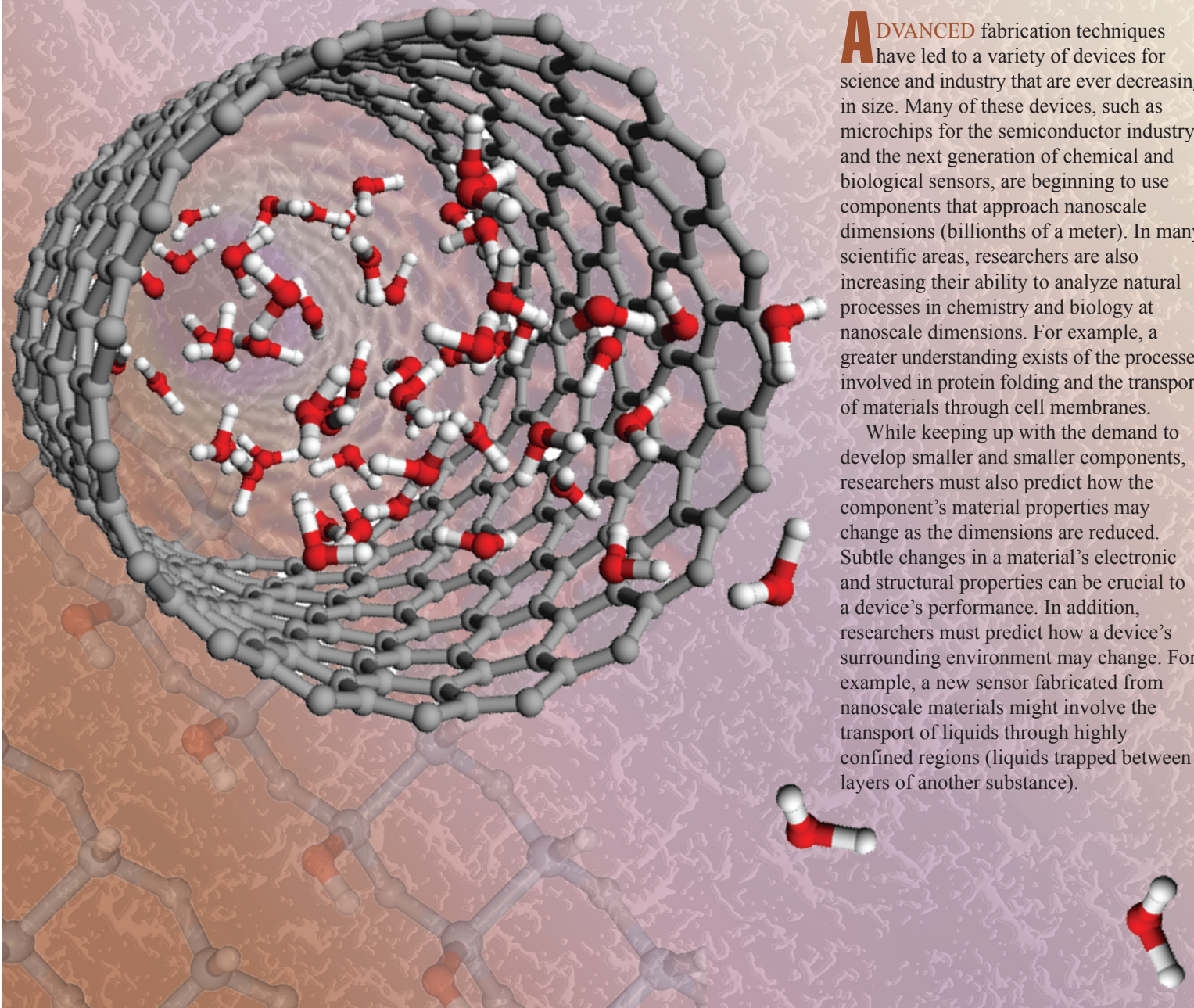
Simulating Materials for Nanostructural Designs

Models of the interaction between water and semiconductor surfaces at the nanoscale show that changes in both affect the performance of nanodevices.



ADVANCED fabrication techniques have led to a variety of devices for science and industry that are ever decreasing in size. Many of these devices, such as microchips for the semiconductor industry and the next generation of chemical and biological sensors, are beginning to use components that approach nanoscale dimensions (billionths of a meter). In many scientific areas, researchers are also increasing their ability to analyze natural processes in chemistry and biology at nanoscale dimensions. For example, a greater understanding exists of the processes involved in protein folding and the transport of materials through cell membranes.

While keeping up with the demand to develop smaller and smaller components, researchers must also predict how the component's material properties may change as the dimensions are reduced. Subtle changes in a material's electronic and structural properties can be crucial to a device's performance. In addition, researchers must predict how a device's surrounding environment may change. For example, a new sensor fabricated from nanoscale materials might involve the transport of liquids through highly confined regions (liquids trapped between layers of another substance).

Lawrence Livermore National Laboratory

Understanding how the structural and dynamic properties of a liquid, such as water, changes as it passes through these confined regions is extraordinarily challenging for both experimentalists and theorists.

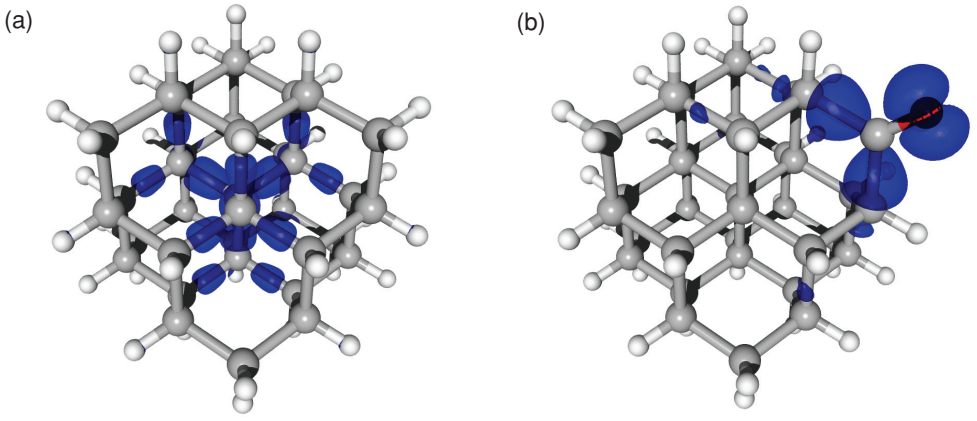
A Livermore team, led by physicist Eric Schwegler, is developing computational tools to simulate the electronic and structural properties of confined water at the nanoscale as it comes into contact with materials such as silicon carbide and graphite sheets. Their work will help researchers predict how the properties of a liquid might be altered in a nanoscale confinement.

Measuring Nanosize Materials

In the past few years, Livermore has conducted research funded by the Laboratory Directed Research and Development (LDRD) Program on a wide range of semiconductor nanostructures—also known as nanodots or quantum dots. Nanodots are tiny atomic structures just a few nanometers in size, about 100,000 times smaller than the width of a human hair. (See *S&TR*, April 2002, pp. 4–10.)

A nanosize quantity of material can have very different basic properties than the same material in its bulk form. Nanodots have unique and interesting properties such as the ability to emit different colors of light depending on their diameter. Because silicon in bulk form is compatible with biological materials, researchers believe the material may be useful in nanosensors to detect biological and chemical warfare agents.

Schwegler, who leads Livermore's Quantum Simulations Group, says, "When reduced to the nanoscale, a material's shape and crystalline structure can change as well as its electronic and optical properties and melting and boiling temperatures." The Livermore team, which includes physicists Francois Gygi, Giulia Galli, and Andrew Williamson and postdoctoral researchers Giancarlo Cicero and David Prendergast, hopes that modeling the interactions of water with potential confining materials, such as silicon carbide, graphite sheets, and carbon nanotubes, will advance theoretical understanding of confined fluids at the nanoscale. The researchers also hope to provide experimentalists with models of



In silicon quantum dots, the wavelength of light that is absorbed depends strongly on the cluster's size and surface chemistry. (a) The purple cloud in this silicon cluster covered with hydrogen atoms represents regions where light will be absorbed. (b) When two of the hydrogen atoms on the surface are replaced by oxygen, the light-absorbing region moves, and the optical properties of the cluster are altered.

Carbon Nanotubes—Small but Strong

Strictly speaking, a nanotube can be any tube with nanoscale dimensions. Nanotubes are most commonly made of carbon, but they have also been produced from materials such as boron nitride and gallium nitride. Carbon nanotubes are unique nanostructures with remarkable electronic and mechanical properties. These cylindrical structures are based on the hexagonal lattice of carbon atoms that form crystalline graphite. An ideal nanotube consists of a network of lattices rolled to form a seamless cylinder. Single-wall nanotubes are the fundamental cylindrical structure and form the building blocks of both multiwall nanotubes (nanotubes within nanotubes) and the ordered arrays of single-wall nanotubes called ropes. In the 1990s, researchers found a way to efficiently produce bundles of single-wall nanotubes. This discovery has provided opportunities for quantitative experimental studies on carbon nanotubes.

The tubes, which can be used as nanoscale wires and electrical components, act as conductors or semiconductors depending on the direction they are rolled. The one-dimensional fibers that compose nanotubes exhibit an electrical conductivity as high as copper, a thermal conductivity as high as diamond, and a strength 100 times greater than steel at one-sixth the weight.

Electronic circuit technology cannot continue to shrink by orders of magnitude and provide corresponding increases in computational power. Nanocomposites, however, offer dramatic opportunities to further advance the downsizing of circuit dimensions and the development of novel computer technologies.

what they should expect to find when examining interactions between water and other materials, such as carbon nanotubes, at similar scales. (See the box on p. 12.)

Researchers have used experimental techniques such as neutron and x-ray diffraction to characterize the properties of bulk water. However, detailed information on liquids confined at the nanoscale has been limited because of the difficulty in probing the solid–liquid interface in nanosize devices. Theoretical and computational studies have also been limited because these complex, multicomponent systems require large-scale simulations to be realistic. Past studies have been restricted to computationally inexpensive models based on classical molecular dynamics (MD).

In classical MD simulations, researchers use calculations that describe the motion of molecules according to forces defined by empirical interaction potentials. These potentials are determined by observing how molecules behave in a given phase at a specific temperature and pressure. Researchers then compute the trajectories of the molecules in small time steps by integrating Newtonian equations of motion. Because empirical potentials describing the interactions between the atoms of the system must be supplied as input before the simulations can be carried out, classical MD is limited in the information it can provide about complex systems whose interactions are not well characterized.

Coupling a Supercomputer and Code

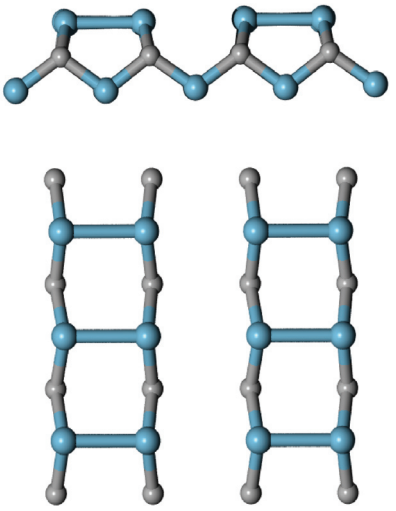
To model complex systems without using predefined empirical potentials, researchers must use codes based on first principles. In 2004, Gygi developed Qbox, a first-principles MD code. First-principles MD simulations use the laws of quantum mechanics to describe the electrons in a system. The data are then used to accurately compute the interactions between atoms without experimental input. The Qbox code calculates the electronic structure of a system using methods based on density functional theory, which defines a molecule's energy and electronic structure in terms of its electron density. Galli, who along with Gygi is now a professor at the University of California at Davis, says, "At the nanoscale, predicting the behavior of water is extraordinarily challenging, and experimental data are sparse. Quantum simulations allow us to make predictions, even if little or no experimental data are available."

Modeling complex interfacial systems with first-principles MD has been challenging even with today's supercomputers. The Livermore group is using the Laboratory's Thunder machine, which can execute 23 trillion operations per second. Thunder is funded by Livermore's Multiprogrammatic and Institutional Computing Initiative, which grants scientists engaged in leading-edge research access to computer time. In 2004, Schwegler's team was awarded one of the largest time allotments on Thunder as part of Livermore's computational grand challenges.

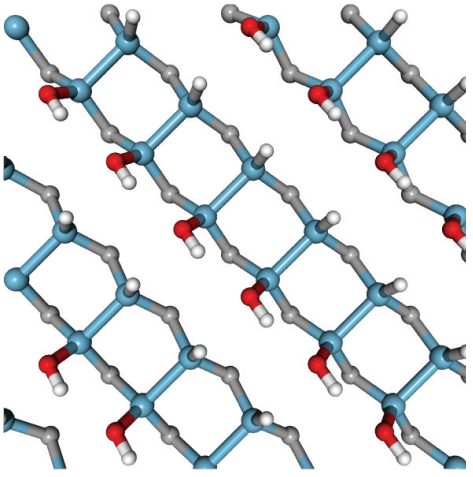
Together, Thunder and the Qbox code can efficiently calculate systems involving hundreds of atoms, allowing researchers to study nanotechnology and biochemistry applications. These same tools are used to conduct research on condensed matter subjected to extreme temperatures and pressures. For example, in 2004, Livermore researchers used Qbox to predict a new melting curve of hydrogen at extremely high pressures. (See *S&TR*, January/February 2005, pp. 4–13.)

Different Reactions to Water

The team used first-principles MD simulations to model the properties of confined liquid water as it interacts with silicon carbide surfaces, graphite sheets, and carbon nanotubes. The models simulated systems containing between 500 and 600 atoms for 20 to 25 picoseconds. Schwegler says, "The combination of a highly optimized and robust code such as



Silicon carbide is composed of alternating layers of carbon (gray) and silicon (blue) atoms.



Silicon atoms (blue) exhibit a hydrophilic (water-binding) characteristic and form bonds with water molecules (red and white). In contrast, carbon atoms (gray) possess a hydrophobic (water-repelling) characteristic and do not easily form bonds with water.

Qbox running on Thunder enabled us to simulate such complex systems."

Surfaces made of silicon carbide were chosen for the study because the material's high electrical conductivity is useful in electronic devices. In addition, the material's high mechanical, thermal, and chemical stability are characteristics that make it a promising candidate for use in biocompatible devices. Silicon carbide is made of alternate layers of carbon and silicon atoms. Consequently, the material has two possible surfaces with quite different electronic and structural properties. These properties have a strong effect on the material's relationship with water. In particular, surfaces rich in carbon atoms have a hydrophobic (water-repelling) character, while surfaces rich in silicon atoms are strongly hydrophilic (water-binding).

The team designed the simulations by "slicing" solid silicon carbide so calculations could be run for surfaces that terminated with either silicon or carbon atoms. For the strongly hydrophilic surfaces that terminated with silicon atoms, the simulation results indicated that water molecules near the surface tend to spontaneously dissociate into a hydrogen or an oxygen–hydrogen group, completely covering the hydrophilic surfaces. In contrast, water molecules approaching the carbon-terminated surfaces remained floating above the silicon carbide, which is characteristic of a hydrophobic interaction.

The team also examined the effects of water confined by carbon graphite sheets and carbon nanotubes, which have hydrophobic surfaces similar to the carbon-terminated silicon carbide slices. By studying how the properties of water change as it is sandwiched between two sheets of graphite or as it fills the interior of a carbon nanotube, the researchers could examine the differences between one- and two-dimensional confinement by a hydrophobic material. Surprisingly, the results indicated that hydrophobic surfaces tend to have a more pronounced effect on the structural and dynamical properties of confined liquid water than do hydrophilic surfaces.

Designing Novel Nanostructures

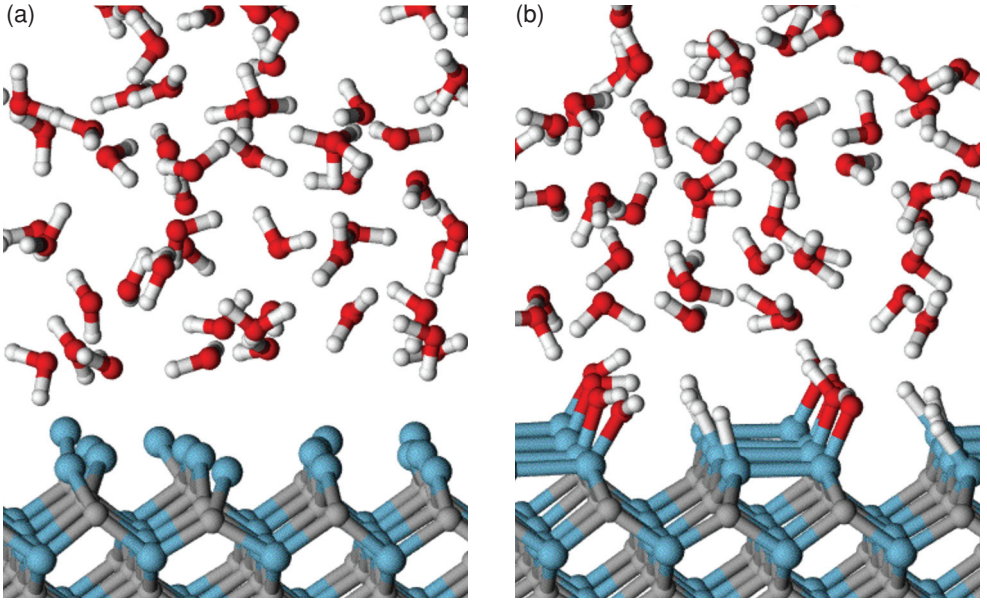
The team's findings suggest that researchers may be able to prepare nanoscale materials with specific hydrophilic and

The Love–Hate Relationship with Water

Why does water bead on some surfaces and not on others? People rely on water to bead rather than be absorbed on raincoats and freshly waxed cars. On the other hand, most forms of life depend on the ability to rapidly transport water through cell walls via membrane channels. These two competing tendencies, which scientists refer to as hydrophobic (water repelling) and hydrophilic (water binding), depend on the material with which the water molecules are interacting.

Scientists take advantage of hydrophilic and hydrophobic tendencies of materials to develop commercial products. For example, laundry soap works because one part of the soap molecule is hydrophilic and the other is hydrophobic. The hydrophilic part allows the hydrophobic fatty acids to come into contact with other hydrophobic substances such as the dirt on the surface being cleaned. When the grime adheres to the soap's fatty acids, it becomes encapsulated in droplets of water. Dirt, oil, and bacteria can then be washed away in this suspended state.

Researchers hope that with a better understanding of how water interacts with a material's properties at the nanoscale, they can design nanoscale devices for many applications in science and industry. The developments will include new sensor technologies for detecting biological threat agents as well as nanofluidic devices for medical applications.



(a) A first-principles simulation shows water molecules (red and white) approaching a layer of silicon carbide that terminates with silicon atoms (blue). (b) As the water molecules approach the material's surface, they dissociate into hydrogen (white) or oxygen–hydrogen groups (white and red) and bond with the silicon carbide.

hydrophobic patterns that are most compatible for an intended purpose. Controlling the properties of a surface by patterning regions with hydrophilic and hydrophobic characteristics is important for DNA and protein attachments.

The simulation studies also strengthen the link between theory and experiment. Experimental measurements of a material's properties often require a theoretical model for interpretation. For example, equations must be used to transform observed x-ray diffraction data into information on the structure of a crystalline material. The Livermore simulations provide structural models that can be used as a basis for transforming the results of specific measurements into detailed information about molecular behavior.

In studies on confined water, of which most experimentalists have little or no experience, the Livermore team is hoping to find unique signatures of the interaction between materials and water confined at the nanoscale. The fingerprints could provide information about properties that are directly related to optical and x-ray absorption experiments—powerful methods used to obtain detailed structural information on the materials interacting with water. For example, simulations using first principles supply accurate structural and dynamic information on such properties as electronic charge densities, polarization effects, and various absorption spectra associated specifically with electronic transitions. Also, by tracking the position of every atom over relevant time scales, the simulations provide useful data on important molecular vibrations in confined water measured during infrared absorption experiments. Prendergast says, "The simulations give us access to structural, electronic, and vibrational properties at the nanoscale that have not yet been accessible by experimental methods."

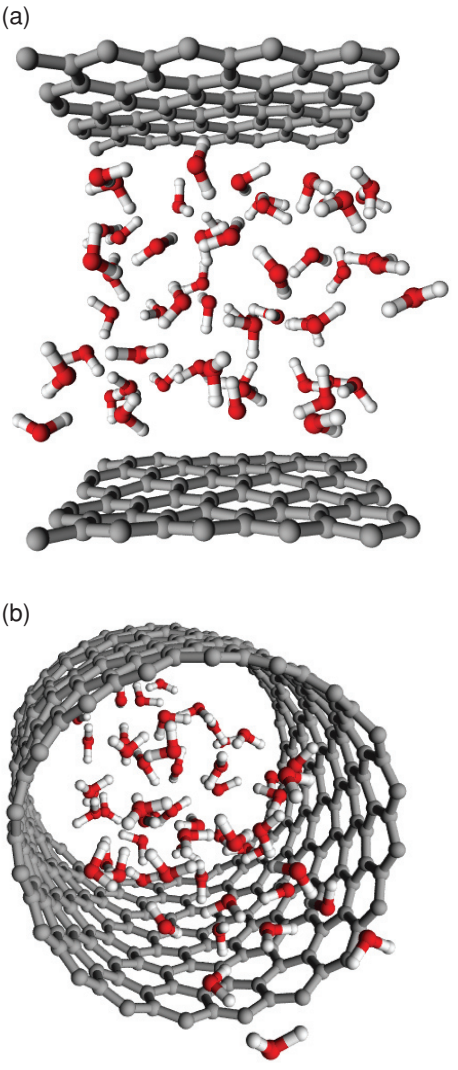
Some of the most promising experiments on water have been based on x-ray absorption measurements, where the interpretations rely heavily on theoretical models. Traditionally, x-ray absorption experiments have been used to probe the electronic structure of high-atomic-number (high-Z) materials such as transition metals and radioactive materials. This research requires the use of high-energy, deep-penetrating x-ray beams from sources such as the Advanced Light Source at Lawrence Berkeley National Laboratory and the Stanford Linear Accelerator Center. However, for materials composed of low-atomic-number (low-Z) elements, such as oxygen, carbon, or hydrogen, the energies at which x rays are absorbed are relatively low and tend to be absorbed by the standard sample containers that are used.

Recently, several experimental groups have devised new methods to probe low-Z materials such as water and other organic molecules. In one method, researchers avoid the use of a container by using a microjet stream of water in a high vacuum to measure the water's absorption of x rays. (See *S&TR*, November 2001, pp. 20–23.) Another approach measures the energy loss of high-energy x rays as they interact with a material encased in beryllium, which is transparent to x rays. Experimentalists can also measure various emission processes that occur after the absorption of x rays, such as the ejection of electrons, ions, and lower energy radiation from the surface of a material.

Detecting Organisms at the Nanoscale

Understanding how hydrogen bonding and hydrophilic and hydrophobic characteristics are affected at the nanoscale will further studies on fluid flow in the confined environments of nanoscale channels. The simulation data provided by Schwegler's team is helping Livermore researchers design nanofluidic devices that will serve the Laboratory's national security mission, which includes developing technologies to detect and identify biological organisms that may have been engineered for the purpose of a biological attack.

Nanofluidic devices move fluids through a maze of microscopic channels that have been fabricated with the lithographic techniques used to make microelectronics. Livermore physicist Sonia Létant is leading an LDRD-sponsored project to synthesize arrays of functionalized pores in silicon membranes that can selectively capture and immobilize an organism ranging from



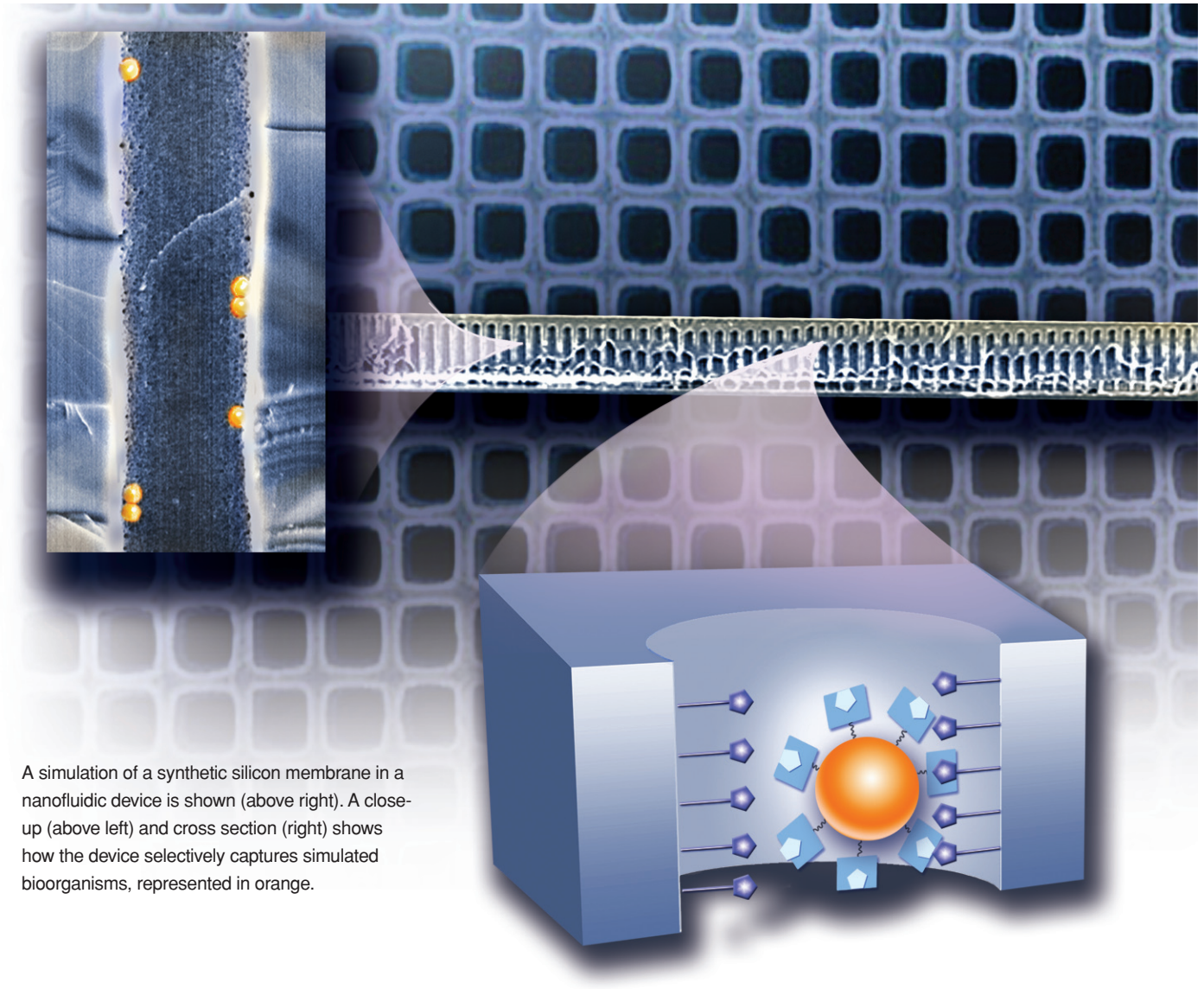
Simulations of water molecules (red and white) confined between (a) carbon graphite sheets and (b) carbon nanotubes demonstrate carbon's hydrophobic tendency.

spores (many micrometers) to viruses (tens of nanometers). The Livermore team is the first to use electrochemical etching to synthesize silicon membranes with pore diameters as small as 30 nanometers. To test the device, the team coated fluorescent microbeads with an antibody and equipped the membranes with a particular antigen. The device selectively captured the matching antibody-coated beads and allowed the remaining beads to flow through the membranes' pores.

To identify organisms, Létant's team is also building a nanofluidic device with a single synthetic pore that mimics an ion channel. As an organism travels through the device, the organism generates a charged current. The amplitude, duration, and shape of the electrical signal provide information on the size, shape, and chemical composition of the organism. Once characterized, the electrical signatures of the organism can be compared to others stored in a database.

In another LDRD-sponsored project, physical chemist Alex Noy is developing innovative nanostructures that can be used for biological-agent detection, water desalination, and kidney dialysis. (See *S&TR*, May 2004, pp. 4–11.) Noy's team is using carbon nanotubes as molecular wire templates to build a nanodevice that can detect bacterial toxins. The team has successfully fabricated and characterized one-dimensional lipid bilayers, which represent a new class of nanostructures. The nanostructures combine carbon nanotubes with synthetic membranes that mimic biological ones.

Physicist Olgica Bakajin is leading an effort to build synthetic membrane pores using carbon nanotubes with diameters between 0.6 and 10 nanometers. The



A simulation of a synthetic silicon membrane in a nanofluidic device is shown (above right). A close-up (above left) and cross section (right) shows how the device selectively captures simulated bioorganisms, represented in orange.

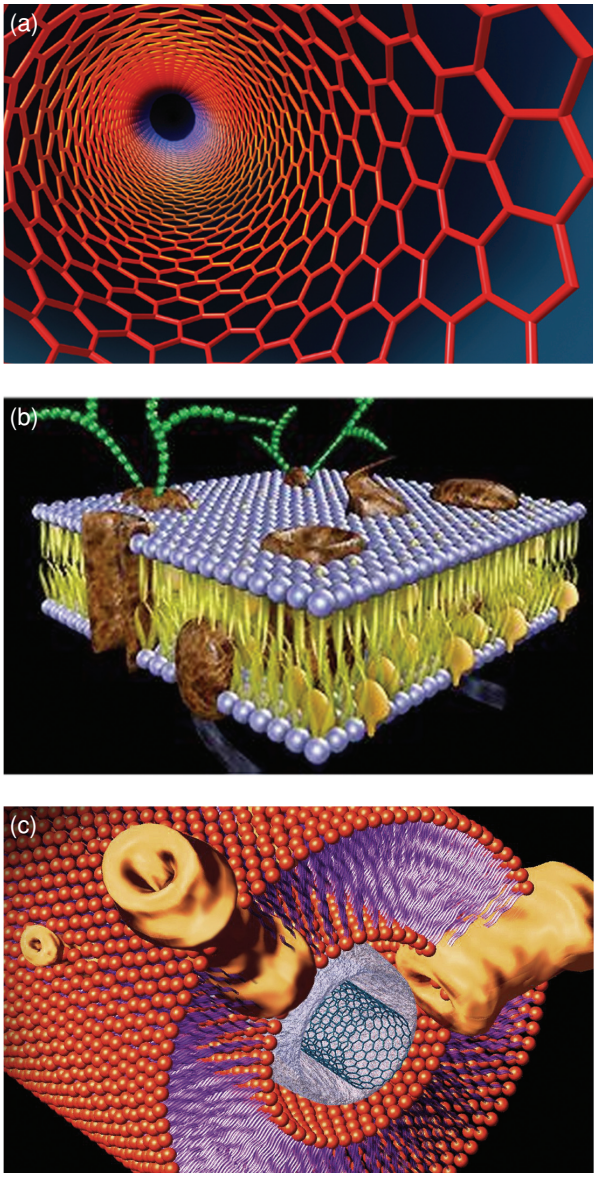
nanodevice will be used to study the effects of confined water not seen in bulk water. Experiments are also under way to characterize the transport of electrolytes through this synthetic membrane for desalination and dialysis applications. The combination of the membrane material's exceptional conductivity and strength and its compatibility with biological materials has resulted in carbon nanotube development becoming a rapidly growing field. Noy says, "Carbon nanotubes are ideal for packaging a large number of individual sensors on the surface of a semiconductor chip. Also, nanotube-based membranes can precisely control how other molecules access the chip components."

Understanding Life's Building Blocks

Protein folding is another research area that will benefit from simulated confined-water studies at the nanoscale because protein-folding experiments are difficult to conduct. (See *S&TR,* December 2004, pp. 12–17.) Computational studies of protein folding have been limited by time-scale capabilities and by the use of predefined parameters fitted to the properties of bulk water. Yet, the confined state of water is expected to be important in folding processes in a hydrophobic environment.

Simulations are playing an increasingly important role in understanding matter at the nanoscale and in predicting the properties of nanomaterials. Understanding the basic science issues involved in the properties of confined liquids is relevant to the development of sensor technologies based on nanoscale materials. Schwegler says, "We expect that we will be able to simulate alternative nanostructures with specific, targeted properties. In turn, this work will open the possibility of designing optimized materials entirely from first principles."

—Gabriele Rennie



By combining (a) carbon nanotubes and (b) synthetic cell membranes, (c) a new class of nanostructures with increased functionality is created. Nanostructures can be used in sensors and potentially in humans.

Key Words: confined water, hydrophilic, hydrophobic, nanofluidic devices, nanostructures, Qbox code, silicon carbide.

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